

**CONDUCTIVE ELECTROLESS PLATING POWDER**

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**Abstract of JP8311655**

**PURPOSE:** To produce a conductive electroless plating powder capable of compounding integrally with a matrix material in excellent dispersibility and capable of imparting always a highly conductive property. **CONSTITUTION:** In the conductive electroless plating powder, a resin powder having such a particle property that it is substantially a spherical powder, whose average grain diameter is within a range of 1-30 $\mu$ m, in which a particle volume ratio in the range of the average grain diameter of  $\pm 20\%$  is  $\geq 70\%$  and the particle volume ratio in a fine powder side in the particles deviated from the average grain diameter of  $\pm 20\%$  is  $\leq 10\%$  is used as a base material, and a metal coating is formed on the surface of the base material by an electroless plating method. A benzoguanamine based resin or a styrene based resin is used preferably as the base material, and the plating layer is preferably a coated film of Ni or Ni-Au.

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(54) 【発明の名称】 導電性無電解めっき粉体

(57) 【要約】

【目的】 マトリックス材料に対し優れた分散性で複合化でき、常に高水準の高導電性能性を付与することができる導電性無電解めっき粉体を提供する。

【構成】 実質的に球状粒子であって、平均粒子径が1～30μmの範囲にあり、平均粒子径±20%範囲の粒分容積比率が70%以上を占め、かつ平均粒子径±20%範囲を外れた粒分のうち微細側の粒分容積比率が10%以下の粒子性状を備える樹脂粉末を基材とし、この基材表面に無電解めっき法により金属被覆を形成してなる導電性無電解めっき粉体。基材としては、ベンゾグアナミン系樹脂またはスチレン系樹脂が好ましく用いられ、めっき層はNiまたはNi-Auの被膜であることが好ましい。

【特許請求の範囲】

【請求項 1】 実質的に球状粒子であって、平均粒子径が  $1 \sim 30 \mu\text{m}$  の範囲にあり、平均粒子径  $\pm 20\%$  範囲の粒分容積比率が  $70\%$  以上を占め、かつ平均粒子径  $\pm 20\%$  範囲を外れた粒分のうち微細側の粒分容積比率が  $10\%$  以下の粒子性状を備える樹脂粉末を基材とし、該基材表面に無電解めっき法により金属被膜を形成してなることを特徴とする導電性無電解めっき粉末。

【請求項 2】 基材となる樹脂が、ベンゾグアナミン系樹脂である請求項 1 記載の導電性無電解めっき粉体。

【請求項 3】 基材となる樹脂が、スチレン系樹脂である請求項 1 記載の導電性無電解めっき粉体。

【請求項 4】 金属被膜が、膜厚  $10 \sim 200 \text{ nm}$  の  $\text{Ni}$  被膜である請求項 1、2 又は 3 記載の導電性無電解めっき粉体。

【請求項 5】 金属被膜が、膜厚  $10 \sim 300 \text{ nm}$  の  $\text{Ni-Au}$  複層被膜である請求項 1、2 又は 3 記載の導電性無電解めっき粉体。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、各種のマトリックス材料に配合した際に優れた分散性ならびに高導電性を付与することができる無電解めっき粉体、特にプラスチック材料に複合化して電子機器類の微小部位を電気的接続する目的に好適な導電性無電解めっき粉体に関する。

【0002】

【従来の技術】導電性を付与したプラスチック材料は、電子機器やその部品の静電防止、電波吸収あるいは電磁波シールド等の部材として広く使用されている。プラスチック材料に導電性を付与する方法としては、従来からマトリックス樹脂成分に微粉状の導電性フィラーを分散複合化する手段が主要な技術とされており、無電解めっき粉体を導電性フィラーとすることも公知である（特開昭 59-182961 号公報、特開昭 60-181294 号公報、特開平 1-242782 号公報等）。また、基材にベンゾグアナミン系樹脂を用いて金属めっきを施した導電性充填剤（特開昭 57-49632 号公報）やスチレン系樹脂を基材として金属めっきを施した導電性充填剤（特開昭 60-12603 号公報）なども提案されている。

【0003】しかしながら、従来技術により得られる導電性めっき粉末は、無電解めっき工程中に基材粒子同士が凝集化し、金属めっき層の膜厚が増すに従って凝集が大きくなり強固となって分散性を損ねる難点がある。導電性粉末の分散性はプラスチック材料に混合した際の導電性能に大きな影響を与えるため、めっき粉末にあってはこの分散性の後退現象が解消されない限り再現性のある高導電性能を期待することができない。

【0004】

【発明が解決しようとする課題】近時、液晶ディスプレイパネルの電極と駆動用 LSI チップの回路基板への接

続、その他微小ピッチの電極端子間の接続など電子機器類の微小部位を電気的接続するための導電材料と対して導電性を付与したプラスチック材料が使用されているが、これらの用途目的には特に高度かつ再現性の良好な導電性能が要求されており、より分散性が改善された導電性フィラーの開発が待たれている。

【0005】導電性無電解めっき粉体の分散性を高めるには、粒径範囲を調整することが有効であるため、篩分けや粉砕処理によって一定の粒子性状に整えることも行われている。しかし、高精度の分級処理を施しても製造過程で生成した凝集体を完全に除去することは困難であり、また粉砕処理を行うと粒子表面の金属被膜が破壊して導電性能の低下を招く。したがって、優れた導電性能を発揮する無電解めっき粉体を得るためには、めっき基材となる樹脂粉末の粒子性状を吟味して良好な分散性および密着性を確保する必要がある。

【0006】本発明者らは、かかる観点からめっき基材となる樹脂粉末の粒子性状について多角的に検討を進めた結果、基材として実質的に球状で、特定範囲の粒子性状を備える樹脂を選択し、この表面に無電解めっき法により金属被覆を施すと、極めて密着性に優れためっき被膜が形成されるうえ、対象マトリックス成分に対する分散性が効果的に改善されて常に高度の導電性能が付与される事実を解明した。

【0007】本発明は上記の知見に基づいて開発されたもので、その目的とするところは、マトリックス成分に対して常に優れた分散性ならびに高導電性を付与することができる高品位の導電性無電解めっき粉末を提供することにある。

【0008】

【課題を解決するための手段】上記の目的を達成するための本発明による導電性無電解めっき粉体は、実質的に球状粒子であって、平均粒子径が  $1 \sim 30 \mu\text{m}$  の範囲にあり、平均粒子径  $\pm 20\%$  範囲の粒分比率が  $70\%$  以上を占め、かつ平均粒子径  $\pm 20\%$  範囲を外れた粒分のうち微細側の粒分比率が  $10\%$  以下の粒子性状を備える樹脂粉末を基材とし、該基材表面に無電解めっき法により金属被膜を形成してなることを構成上の特徴とする。

【0009】本発明において、無電解めっき基材として使用する樹脂の種類には格別の制約はない。使用可能な樹脂類としては、例えばポリエチレン、ポリ塩化ビニル、ポリプロピレン、ポリスチレン、ポリイソブチレン等のポリオレフィン、スチレン-アクリロニトリルコポリマー、アクリロニトリル-ブタジエン-スチレンターポリマー等のオレフィンコポリマー、ポリアクリレート、ポリメチルメタクリレート、ポリアクリルアミド等のアクリル酸誘導体、ポリ酢酸ビニル、ポリビニルアルコール等のポリビニル化合物、ポリアセタール、ポリエチレングリコール、ポリプロピレングリコール、エポキシ樹脂等のエーテルポリマー、ベンゾグアナミン、尿

素、チオ尿素、メラミン、アセトグアナミン、ジシアンアミド、アニリン等のアミノ化合物とホルムアルデヒド、パラホルムアルデヒド、アセトアルデヒド、グリオキザールのようなアルデヒド類とからなるアミノ系樹脂、ポリウレタン、ポリエステル、含弗素樹脂、ニトリル系樹脂などを挙げることができる。しかし、これらの中では例えばベンゾグアナミン・ホルムアルデヒド樹脂またはベンゾグアナミン・メラミン・ホルムアルデヒド樹脂などのベンゾグアナミン系樹脂、もしくはポリスチレン樹脂に代表されるスチレン系樹脂が好適に用いられる。

【0010】このうちベンゾグアナミン系樹脂は、特公昭46-9420号公報、特公昭52-27679号公報、特開昭52-16594号公報または特開昭52-51493号公報に開示されている方法によって製造することができる。具体的には、ベンゾグアナミンもしくはベンゾグアナミンとメラミンとからなる混合物を例えばホルマリンに添加してpHを5~10に調整し、50~100℃の温度で反応生成物が疎水化するまで反応させ、反応終了後に適当な保護コロイド溶液を反応生成物100重量部に対して1~30重量部の量比で攪拌下に加えて乳化させ、次いで重合触媒の存在下に50~100℃の温度で乳化状態で重合硬化させる方法により微細かつ実質的に球状の粒子として得ることができる。

【0011】一方、スチレン系樹脂はスチレンを主体とする重合体であるが、スチレンと少量の多官能性単量体との共重合による架橋重合体であってもよい。スチレンと共重合可能な単量体としては、アクリル酸エステル、メタクリル酸エステル、不飽和カルボン酸、アクリロニトリル、ブタジエンなどが挙げられる。共重合して架橋重合体を形成する多官能性単量体は、例えばジビニベンゼン、多価アルコールのジまたはトリ（メタ）アクリル酸エステルなどである。これらの単量体、ラジカル重合開始剤および懸濁安定剤を添加した混合液を加熱下で攪拌することにより微細で実質的に球状のスチレン系樹脂粉末を得ることができる。

【0012】上記の樹脂基材は、粒子形状として実質的に球状の粉末が用いられる。実質的に球状とは、完全な球形のほか、楕円形のような球形に近い形状を含むことを意味し、好ましくはワーデルの球形度として0.5~1.0の範囲にある球状形態を呈する粉末が対象となる。ワーデルの球形度とは、粒子の球形度を（粒子の投影面積に等しい円の直径）／（粒子の投影像に外接する最小円の直径）で測定される指数で、この指数が1.0に近似するほど真球体に近い粒子であることを示す。この球形度が0.5未満では粉末形状が鋭利な突片を呈することが多く、めっき被膜の密着性を損ねたり分散性を減退させる原因となる。

【0013】樹脂基材の粒子性状としては、平均粒子径が1~30μmの範囲にあり、平均粒子径±20%範囲

の粒分容積比率が70%以上を占め、かつ平均粒子径±20%範囲を外れた粒分のうち微細側の粒分容積比率が10%以下のものが選択使用される。

【0014】平均粒子径を1~30μmの範囲に限定する理由は、平均粒子径が1μm未満の超微細粒子を得ることは実質的に困難であり、また30μmを越えると比表面積が低下して導電性能を減退させるからである。より好ましい平均粒子径の範囲は、5~10μmである。この平均粒子径に対し±20%の粒子径範囲における粒分容積比率が70%を下回ると粒度分布がブロード化して均一な分散性を損ね、また平均粒子径±20%範囲を外れた粒分のうち微細側の粒分容積比率が10%を越えると微細粒子が増加して無電解めっき工程中での凝集が生じ易くなり、結果的にめっき層を密着性や分散性を低下させる要因となる。より好ましい粒度分布は、平均粒子径±20%範囲の粒分容積比率が90%以上で、平均粒子径±20%範囲を外れた粒分のうち微細側の粒分容積比率が1%以下である。

【0015】上記の粒子性状を備える樹脂基材には、表面に無電解メッキ法による金属被膜が形成される。被覆する金属は、無電解めっき操作が可能な導電性金属、例えばAu、Ag、Co、Cu、Ni、Pd、Pt、Snなどが対象となり、これら金属は合金であってもよく、2種以上の複層被覆であってもよい。しかし、本発明の目的には、金属被膜がNi被膜またはNi-Au複層被膜であることが好ましい。Ni被膜は基材樹脂粒子と強固に密着して耐剥離性の良好な無電解めっき層を形成することができるうえ、その上面にAuを複層形成するような場合に上層のめっき被膜層との強固な結合性を確保する中間層として有効に機能する有利性がある。また、Ni-Au複層被膜にすると、単独被膜に比べて導電性能を一層向上させることができる。形成する無電解めっき層の好ましい膜厚は、単層被膜では10~200nm、複層被膜では10~300nmの範囲であるが、これに制限されるものではない。

【0016】本発明に係る導電性無電解めっき粉体は、実質的に球状で特定の粒子性状を備える樹脂粉末を基材とし、該基材の表面にパラジウムイオンを捕捉させたのち、これを還元してパラジウムを基材面に担持させる触媒化処理工程と、触媒化処理を施した基材の水性スラリーに錯化剤を添加して十分に分散させ、ついで金属無電解めっき液を少なくとも2液に分別添加して金属被膜を形成する無電解めっき工程を施すことによって製造することができる。また、複層被膜を形成するには、前記の工程で金属被膜を形成した基材を対象に他の金属無電解めっきを施し、初期金属めっき層の上面に他の金属被膜を被覆する方法が採られている。

【0017】無電解めっき法の具体的手段は、次のように行われる。まず、基材となる基材樹脂粒子の表面に触媒捕捉能を付与する改質処理を行う。触媒捕捉能とは、

触媒化処理工程において基材表面がパラジウムイオンをキレートまたは塩として捕捉しうる機能であり、改質化は特開昭61-64882号公報記載の方法、すなわちアミノ基置換オルガノシラン系カップリング剤やアミン系硬化剤により硬化するエポキシ系樹脂を用いて行うことができる。

【0018】触媒化処理工程は、改質化により触媒捕捉能を付与した基材を塩化パラジウムの希薄な酸性水溶液に十分に分散させて表面上にパラジウムイオンを捕捉させ、ついで捕捉させたパラジウムイオンを還元処理して基材粒子の表面にパラジウムを担持させる方法で行われる。この際、塩化パラジウム水溶液の濃度は、0.05～1g/lの範囲とし、還元剤には次亜リン酸ナトリウム、水酸化ほう素ナトリウム、水素化ほう素カリウム、ジメチルアミンボラン、ヒドラジンまたはホルマリンなどが用いられる。還元剤の添加量は基材の粒径により異なるが、概ね水溶液に対して0.01～10g/lの範囲が適当である。

【0019】無電解めっき工程は、第1段として触媒化処理を施した基材粒子を水に十分均一に分散し、分散濃度が2～500g/l、好ましくは5～300g/lの水性スラリーを調製する。分散操作には、通常攪拌、高速攪拌あるいはコロイドミルまたはホモジナイザーのような剪断分散装置を用いて行うことができる。ついで水性スラリーに錯化剤を添加して十分に分散させる。錯化剤としては、例えばクエン酸、ヒドロキシ酢酸、酒石酸、リンゴ酸、乳酸、グルコン酸またはそのアルカリ金属塩やアンモニウム塩などのカルボン酸(塩)、グリシンなどのアミノ酸、エチレンジアミン、アルキルアミンなどのアミン酸、その他のアンモニウム、EDTA、ピロリン酸(塩)など、金属イオンに対し錯化作用のある化合物の少なくとも1種が用いられる。錯化剤は通常水溶液の状態に添加されるが、その濃度は1～100g/l、好ましくは5～50g/lの範囲に設定する。この段階での好ましい水性スラリーのpHは、4～14の範囲である。

【0020】このようにして調製した水性スラリーに、無電解めっき液として金属塩、次亜リン酸ナトリウムおよび水酸化ナトリウムの各水溶液を、少なくとも2液にしてそれぞれ個別かつ同時に分別添加することにより無電解めっき反応を行う。水性スラリーに無電解めっき液を添加すると速やかにめっき反応が始まるが、その添加量を調整することにより形成される金属被膜を所望の膜厚に制御することができる。無電解めっき液の添加終了後、水素ガスの発生が完全に認められなくなってから暫く液温を保持しながら攪拌を継続して反応を完結させる。

【0021】上記の工程により金属被膜が濃密で連続的薄膜として形成されるが、さらにその表面に他の金属めっき処理を施すことにより、一層導電性能に優れた複層被膜を形成することができる。例えばAu被膜の形成に

おいては、EDTA-4Na、クエン酸-2Naのような錯化剤およびシアン化金カリウムに水酸化ナトリウム水溶液でpHを弱酸性領域に調整した加温無電解めっき液に、前記めっき粉末を攪拌しながら添加して分散懸濁液としたのち、シアン化金カリウム、EDTA-4Naおよびクエン酸-2Naの混合水溶液と、水素化ほう素カリウム、水酸化ナトリウムの混合水溶液を別個に添加してめっき反応させる操作によって行われる。以下、同様に常法により後処理することにより製品として回収する。

【0022】このようにして無電解めっき法により金属被覆が施された導電性無電解めっき粉体は、被覆金属層が緻密で連続性の薄膜として形成されているため、その粒子性状は基材樹脂粒子に比べて僅かに粒径が大きくなる程度で、粒度分布等実質的に相違をもたらすことはない。

【0023】

【作用】本発明は、導電性金属を無電解めっきする基材となる樹脂粉末として、粒子形態が実質的に球状を呈し、平均粒径が1～30μmの範囲にあり、平均粒径±20%範囲の粒分容積比率が70%以上を占め、かつ平均粒径±20%範囲を外れた粒分のうち微細側の粒分容積比率が10%以下の粒子性状を備えるものを選択使用した点に主要な特徴がある。

【0024】このうち、実質的に球状の粒子形態は優れた流動性があり、個々の粒子相互が凝集化する現象を防止するとともに均一なめっき層を形成するために有効に機能する。平均粒径1～30μmの範囲は、比表面積が大きな微細粒子として無電解めっき粉体をマトリックスに分散複合させた際に導電性能を高めるために寄与する。平均粒径±20%範囲の粒分容積比率が70%以上を占め、かつ平均粒径±20%範囲を外れた粒分のうち微細側の粒分容積比率が10%以下の限定は、粒度分布がシャープで凝集化を促進する微細粒分が相対的に少ない粒子性状であり、無電解めっき金属の密着性を高めると同時にめっき粉体の分散性を著しく改善する作用を営む。このような作用が相俟って、マトリックス材料に対して常に分散性よく配合でき、かつ高導電性能の付与ができる無電解めっき粉体を提供することが可能となる。

【0025】

【実施例】以下、本発明の実施例を比較例と対比して具体的に説明する。

【0026】実施例1～5、比較例1～4

(1) 基材樹脂粉末：基材として、ワードルの球形度が0.5以上の実質的に球状の粉末であって、表1に示す粒子性状のベンゾグアナミン・ホルムアルデヒド樹脂(BA)、ベンゾグアナミン・メラミン・ホルムアルデヒド樹脂(BMA)およびポリスチレン樹脂(PS)を用いた。

[0027]

\* \* [表1]

例No.	基材樹脂	平均粒子径 ( $\mu\text{m}$ )	平均粒子径 $\pm 20\%$ 範囲の粒分容積比 率 (%)	平均粒子径 $\pm 20\%$ 範囲外の微細側粒 分容積比率 (%)
実施例 1	BA	7.8	99.5	0.05
" 2	BA	4.6	99.0	0.04
" 3	BMA	7.8	99.5	0.05
" 4	BMA	4.6	99.0	0.04
" 5	PS	10.3	80.2	2.30
比較例 1	BA	9.6	44.7	25.6
" 2	BMA	15.4	59.5	14.8
" 3	BMA	3.3	59.2	13.8
" 4	PS	9.2	36.1	33.8

〔表注〕 BA ; ベンゾグアナミン・ホルムアルデヒド樹脂、BMA ; ベンゾグアナミン・メラミン・ホルムアルデヒド樹脂、PS ; ポリスチレン樹脂。

〔0028〕 (2) Ni 無電解めっき処理 ; 表1の各基材樹脂粉末10gを、コンディショナー液〔シブレイ製、"クリーナーコンディショナー231"〕40ml/l水溶液200mlに攪拌しながら投入し、引き続き5分間攪拌処理して表面改質を行った。水溶液を濾過し、1回リバルブ水洗した基材樹脂粉末を常温の1g/l塩化第一錫水溶液200mlに5分間浸漬し、濾過・洗浄して増感処理を施した。ついで、0.1ml/l塩化パラジウム水溶液および0.1ml/lの塩酸からなる触媒液200mlに攪拌しながら投入し、引き続き5分間攪拌処理してパラジウムイオンを捕捉させた。水溶液を濾過し、1回リバ※30

20※イブ水洗した基材粉体を、常温の1g/l次亜リン酸ナトリウム水溶液に5分間浸漬して還元処理を施し、基材表面にパラジウムを担持させた。基材を65℃の温度に加熱した表2に示す各錯化剤水溶液に攪拌しながら添加し、十分に攪拌分散させて水性スラリーを調製したのち、表3に示すNi無電解めっき液をa液とb液に分けて各々80mlを5ml/分の添加速度で攪拌しながら同時に添加した。

〔0029〕  
〔表2〕

例No.	錯化剤の種類	濃度(g/l)	pH
実施例 1	リンゴ酸ソーダ	10	6
" 2	グリシン	20	8
" 3	酒石酸ソーダ	10	7
" 4	クエン酸ソーダ	5	7
" 5	酢酸ソーダ	20	6
比較例 1	リンゴ酸	10	6
" 2	リンゴ酸	10	6
" 3	酒石酸ソーダ	10	7
" 4	酒石酸ソーダ	10	7

[0030]

〔表3〕

Ni無電解めっき液の組成	濃度(g/l)	モル比
a液；硫酸ニッケル	224	1
b液；次亜リン酸ナトリウム 水酸化ナトリウム	226 119	2.5 3.5

【0031】Ni無電解めっき液の全量を添加後、水素の発泡が停止するまで65℃の温度を保持しながら攪拌を継続した。ついで、めっき液を濾過し、濾過物を3回リバルブ洗浄したのち、真空乾燥機で100℃で乾燥してNi被膜を有する粉末を得た。めっき反応後の濾液はいずれも無色透明であり、供しためっき液は完全にめっき反応に消費されたことが認められた。得られたNi無電解めっき粒子につき、電子顕微鏡で観察したところ、凝集粒子が殆ど存在しない独立した粒子であって、いずれも微細なNi金属粒子による均質で平滑な被覆層を呈する実質的に球状粒子であり、めっき被膜が濃密で連続的被膜として形成されていることが確認された。

【0032】(3) Au無電解めっき処理；上記の工程で得られたNi無電解めっき粒子10.0gを、EDTA\*

\*-4Na(10g/l)、クエン酸-2Na(10g/l)およびシアン化金カリウム(3.0g/l、Auとして2.1g/l)からなる組成で水酸化ナトリウム水溶液によりpH6に調整した液温60℃の無電解めっき液(A液)に攪拌しながら添加し、10分間Auめっき処理を施した。ついで、シアン化金カリウム(10g/l、Auとして6.8g/l)、EDTA-4Na(10g/l)およびクエン酸-2Na(10g/l)の混合水溶液(B液)と、水素化ほう素カリウム(30g/l)、水酸化ナトリウム(60g/l)の混合水溶液(C液)を送液ポンプを通して個別かつ同時に20分間で添加した。この際のA液量、B液量およびC液量は、表4に示す量比に設定した。

【0033】

【表4】

例No.	A液量 (ml)	B液量 (ml)	C液量 (ml)
実施例1	152	47	47
" 2	255	79	79
" 3	152	47	47
" 4	255	79	79
" 5	152	47	47
比較例1	152	47	47
" 2	152	47	47
" 3	152	47	47
" 4	152	47	47

【0034】引き続き、液を濾過し、濾過物を3回リバルブ洗浄した後、熱風乾燥機で100℃の温度で乾燥してNi被膜上にAu無電解めっき被覆処理を施し、基材面にNi-Auの複層被膜を形成した。図1は実施例2により得られたNi-Auの複層被膜による導電性無電解めっき粉体(平均粒径：4.84μm)の粒子構造を示した電子顕微鏡写真(倍率：約330倍)であり、図2は比較例4により得られたNi-Auの複層被膜による導電性無電解めっき粉体(平均粒径：9.8μm)の粒子構造を示した電子顕微鏡写真(倍率：約330倍)である。

【0035】(3) 物性評価；このようにして得られた導電性無電解めっき粉体の平均粒径、Ni無電解めっき処理後のNi被膜の膜厚および導電性、分散性、耐剥離性、Ni-Au複層被膜の膜厚および導電性、分散性、

耐剥離性をそれぞれ測定評価し、その結果を表5および表6に示した。なお、各物性評価は次の方法によって行った。

40 【0036】①めっき粉体の平均粒子径の測定；コールターカウンター法およびレーザー回折法により測定した。

②めっき膜厚の算出；めっき膜厚は下式により算出した。

$$A = \frac{[(r+t)^3 - r^3] d_1}{r_2 d_2}$$

但し、rは基材粒子の半径(μm)、tはめっき膜厚(μm)、d<sub>1</sub>はめっき膜の比重、d<sub>2</sub>は基材粒子の比重である。

50 ③導電性の測定；めっき粉末1.5gを垂直に立てた内

径10mmの樹脂製円筒内に入れ、5kgの荷重をかけた状態で上下電極間の電気抵抗を測定する方法で行った。

【0037】④分散性の測定：めっき粉末0.1gを100mlのビーカーに入れ、トルエン50mlを加え、ミクロスパーテルでかき混ぜながら、1分間超音波洗浄機（本多電子（株）製、28kHz,100W）で処理する。処理したスラリーを、ミクロスパーテルで取り出し、スライドガラス上に直径1cmとなる程度に広げる。スライドガラスを金属顕微鏡（オリンパス製、500倍）の台にセットし、透過光を照射してから1分後の様子を撮影する。評価方法は、上記方法で撮影した写真20視野で平均粒子径の縦・横方向で5倍以上の大きさでめっき粒子が凝集している数を計測し、下記の基準で評価判定する。

5個以下…◎、5～10個…○、10個以上…×

【0038】⑤密着性の測定：めっき粉末2.2g、ジルコニアビーズ90gを100mlのマヨネーズビンに入\*

＊れ、ホールビベットでトルエン10mlを加える。攪拌機（スリーワンモーター）で10分間400rpmで10分間攪拌する。終了後、ビベットで試料溶液を吸い上げ、スライド上に直径約1cmになるように広げる。トルエンが蒸発してから、分散剤を1滴たらし、スパチラで均一に広げる。金属顕微鏡で観察し、5視野透過撮影（500倍）し、最もめっき層剥離の激しい視野を観察し、その剥離数から下記の判定基準で評価する。

2個以下…◎、2～10個…○、10個以上…×

【0039】比較例5

比較例1で作製した無電解めっき粉体を、アルミナボールを入れたボールミル中で基材粒子とほぼ同等の粒子分布を示すまで乾式粉碎を行い、粉体の性状を測定評価し、表5および表6に併載した。

【0040】

【表5】

例No.	N1無電解めっき粉末の物性				
	平均粒子径 ( $\mu\text{m}$ )	膜厚 (nm)	電気抵抗値 ( $\Omega\text{cm}$ )	分散性	密着性
実施例1	8.1	115	$1.2 \times 10^{-1}$	◎	◎
＃2	4.9	97	$3.2 \times 10^{-1}$	◎	◎
＃3	7.9	121	$1.0 \times 10^{-1}$	◎	◎
＃4	5.1	113	$4.8 \times 10^{-1}$	◎	◎
＃5	14.7	152	$1.8 \times 10^{-1}$	○	◎
比較例1	20.9	150	$2.9 \times 10^{-1}$	×	◎
＃2	31.9	290	$4.0 \times 10^{-1}$	×	◎
＃3	13.2	110	$2.9 \times 10^{-1}$	×	◎
＃4	10.0	150	$7.2 \times 10^{-1}$	○	×
＃5	28.6	170	$2.0 \times 10^{-1}$	×	◎

【0041】

【表6】



例No.	Ni-Au無電解めっき粉末の物性				
	平均粒子径 ( $\mu\text{m}$ )	膜厚 (nm)	電気抵抗値 ( $\Omega\text{cm}$ )	分散性	密着性
実施例1	8.2	20	$2.0 \times 10^{-3}$	◎	◎
" 2	4.84	22	$3.0 \times 10^{-3}$	◎	◎
" 3	8.0	20	$1.0 \times 10^{-3}$	◎	◎
" 4	4.82	20	$2.0 \times 10^{-3}$	◎	◎
" 5	17.0	20	$0.9 \times 10^{-3}$	○	◎
比較例1	28.6	18	$1.0 \times 10^{-3}$	×	◎
" 2	44.0	20	$1.0 \times 10^{-3}$	×	◎
" 3	16.8	21	$2.0 \times 10^{-3}$	×	◎
" 4	9.8	18	3.5	○	×
" 5	29.4	20	$1.0 \times 10^{-3}$	×	◎

【0042】表5および表6の結果から、実施例による導電性無電解めっき粉体は本発明の要件を外れる比較例に比べて導電性、分散性、密着性ともに優れており、特に分散性が著しく改善されていることが認められる。

#### 【0043】実施例6

(1) Ag無電解めっき処理：表1に示した実施例1と同一のベンゾグアナミン・ホルムアルデヒド樹脂粉末を基材とし、この樹脂粉末10gをコンディショナー液〔シブレイ製、"クリーナーコンディショナー231"〕40ml/l水溶液200mlに攪拌しながら投入し、引き続き5分間攪拌処理して表面改質を行った。水溶液を濾過し、1回リバルブ水洗した基材粉末を常温の1g/l塩化第一錫水溶液200mlに5分間浸漬し、濾過・洗浄して増感処理を施した。次いで、0.1ml/l塩化パラジウム\*

\*水溶液および0.1ml/lの塩酸からなる触媒化液200mlに攪拌しながら投入し、引き続き5分間攪拌処理してパラジウムイオンを捕捉させた。水溶液を濾過し、1回リバルブ水洗した基材粉末を、常温の1g/l次亜リン酸ナトリウム水溶液に5分間浸漬して還元処理を施し、基材表面にパラジウムを担持させた。次いで、水酸化ナトリウムおよびシアン化ナトリウム各4g/lを含む液を80℃に加熱した液中に分散させ、実施例1と同様にして表7に示すAg無電解めっき液をa液とb液に分けて各々80mlを5ml/分の添加速度で攪拌しながら同時に添加した。

#### 【0044】

##### 【表7】

Ag無電解めっき液の組成	濃度 (g/l)	モル比
a液；シアン化銀カリウム	150	1
b液；水酸化ホウ素ナトリウム 水酸化ナトリウム	36 120	1.2 4.0

【0045】Ag無電解めっき液の全量を添加したのち、水素の発泡が停止するまで65℃の温度を保持しながら攪拌を継続した。ついで、めっき液を濾過し、濾過物を3回リバルブ洗浄し、真空乾燥機で100℃で乾燥してAg被膜を有する粉末を得た。めっき反応後の濾液はいずれも無色透明であり、供しためっき液は完全にめっき反応に消費されたことが認められた。得られたAg無電解めっき粒子につき、電子顕微鏡で観察したところ、いずれも微細なAg金属粒子による均質で平滑な被覆層を呈する球状粒子であり、めっき被膜が濃密で実質

的に連続被膜として形成されていることが確認された。

【0046】(2) Au無電解めっき処理：上記(1)の工程で得られたAg無電解めっき処理粉体に対し、実施例1と同一操作で無電解Auめっき処理を行った。

【0047】このようにして得られたAg-Au複層被膜を有する導電性無電解めっき粉体を実施例1と同様にして各種の物性を評価し、その結果を表8に示した。

#### 【0048】実施例7

基材樹脂粉末を実施例2と同一のベンゾグアナミン・ホルムアルデヒド樹脂に代え、その他は実施例6と同一の

操作によりAg-Au複層被膜を有する導電性無電解めっき粉体を作製した。この導電性無電解めっき粉体を実施例1と同様にして各種の物性を評価し、その結果を表8に併載した。

【0049】比較例6

基材として、平均粒子径9.6 $\mu\text{m}$ 、平均粒子径 $\pm 20$

%範囲の粒分容積比率が44.7%、平均粒子径 $\pm 20$

%範囲を外れた粒分のうち微細側の粒分容積比率が2 \*

\* 5.6%の実質的に球状のベンゾグアナミン・メラミン・ホルムアルデヒド樹脂粉末を用い、実施例6と同一の操作によりAg-Au複層被膜を有する導電性無電解めっき粉体を作製した。この導電性無電解めっき粉体を実施例1と同様にして各種の物性を評価し、その結果を表8に併載した。

【0050】

【表8】

例No.	Ag-Au無電解めっき粉末の物性					
	平均粒子径 ( $\mu\text{m}$ )	膜厚(nm)		電気抵抗値 ( $\Omega\text{cm}$ )	分散性	密着性
		Ag	Au			
実施例6	8.2	100	21	$1 \times 10^{-3}$	◎	◎
7	4.7	88	21	$1 \times 10^{-3}$	◎	◎
比較例6	31.4	110	22	$1 \times 10^{-3}$ 以下	×	◎

【0051】

【発明の効果】以上のとおり、本発明によれば基材として実質的に球状であって、粒度分布がシャープな特定範囲の微粒子樹脂粉末を用いて表面に無電解金属めっき層を被覆することにより、緻密で連続的なめっき層が密着性よく被着し、かつ複合マトリックス材料に対する分散性に優れる導電性無電解めっき粉体を提供することが可能となる。したがって、例えば液晶ディスプレイパネル用の精密導電材のような高度の導電性能が要求される用途に極めて有用である。

※30

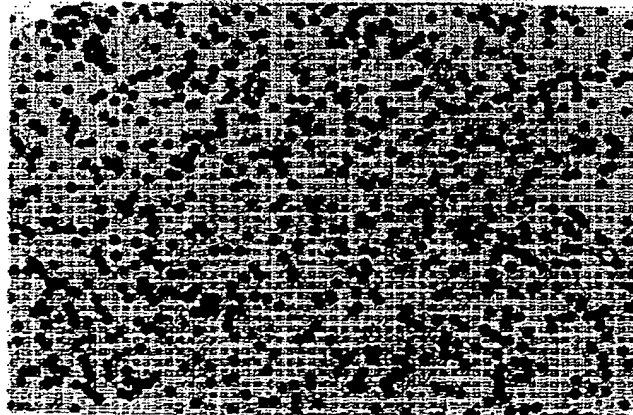
※【図面の簡単な説明】

【図1】実施例2により得られたNi-Auの複層被膜による導電性無電解めっき粉体（平均粒径：4.84 $\mu\text{m}$ ）の粒子構造を示した電子顕微鏡写真（倍率：約330倍）である。

【図2】比較例4により得られたNi-Auの複層被膜による導電性無電解めっき粉体（平均粒径：9.8 $\mu\text{m}$ ）の粒子構造を示した電子顕微鏡写真（倍率：約330倍）である。

【図1】

断面代用写真



【図2】



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(54) CONDUCTIVE ELECTROLESS PLATING POWDER

## (57)Abstract:

PURPOSE: To produce a conductive electroless plating powder capable of compounding integrally with a matrix material in excellent dispersibility and capable of imparting always a highly conductive property.

CONSTITUTION: In the conductive electroless plating powder, a resin powder having such a particle property that it is substantially a spherical powder, whose average grain diameter is within a range of 1-30 $\mu$ m, in which a particle volume ratio in the range of the average grain diameter of  $\pm 20\%$  is  $\geq 70\%$  and the particle volume ratio in a fine powder side in the particles deviated from the average grain diameter of  $\pm 20\%$  is  $\leq 10\%$  is used as a base material, and a metal coating is formed on the surface of the base material by an electroless plating method. A benzoguanamine based resin or a styrene based resin is used preferably as the base material, and the plating layer is preferably a coated film of Ni or Ni-Au.

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## CLAIMS

[Claim(s)]

[Claim 1] It is a spherical particle substantially and mean particle diameter is 1-30 micrometers. Conductive nonelectrolytic plating powder which uses as a base material the resin powder with which the grain partial-volume ratio by the side of detailed is equipped with the shape of 10% or less of corpouscular character among those for the grain which it is in the range, and the grain partial-volume ratio of \*\*20% range of mean particle diameter occupied 70% or more, and separated from \*\*20% range of mean particle diameter, and is characterized by coming to form a metal coat in this base material front face by the nonelectrolytic plating method.

[Claim 2] Conductive nonelectrolytic plating fine particles according to claim 1 whose resin used as a base material is benzoguanamine system resin.

[Claim 3] Conductive nonelectrolytic plating fine particles according to claim 1 whose resin used as a base material is styrene resin.

[Claim 4] Conductive nonelectrolytic plating fine particles according to claim 1, 2, or 3 whose metal coat is a nickel coat of 10-200nm of thickness.

[Claim 5] Conductive nonelectrolytic plating fine particles according to claim 1, 2, or 3 whose metal coat is a nickel-Au double layer coat of 10-300nm of thickness.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the nonelectrolytic plating fine particles which can give the dispersibility and high conductivity ability which were excellent when it blended with various kinds of matrix materials, especially the suitable conductive nonelectrolytic plating fine particles for the object which compound-izes to plastic material and carries out electrical installation of the minute part of electronic equipment to it.

[0002]

[Description of the Prior Art] The plastic material which gave conductivity is widely used as members, such as electrostatic prevention of electronic equipment and its component, electric-wave absorption, or electromagnetic wave shielding. It is also well-known for a means to form a conductive fine-like filler into distributed compound for a matrix resin component to be made into main techniques from the former as an approach of giving conductivity to plastic material and to make nonelectrolytic plating fine particles into a conductive filler (JP.59-182961A, a JP.60-181294A official report, JP.1-242782A official report, etc.). Moreover, the conductive bulking agent (JP.60-12603A) which performed metal plating by using as a base material the conductive bulking agent (JP.57-49832A) and styrene resin which used benzoguanamine system resin for the base material, and performed metal plating is proposed.

[0003] However, base material particles condensation-ize the conductive plating powder obtained by the conventional technique in a nonelectrolytic plating process, and it has the difficulty that condensation becomes it is large and firm and spoils dispersibility as the thickness of a metal plating layer increases. Since the dispersibility of conductive powder has big effect on the conductive ability at the time of mixing to plastic material, if it is in plating powder, unless the retreat phenomenon of this dispersibility is canceled, it cannot expect reproducible high conductivity ability.

[0004]

[Problem(s) to be Solved by the Invention] Although the plastic material which received with the electrical conducting material for carrying out electrical installation of the minute part of electronic equipment, such as connection with the electrode of a liquid crystal display panel and the circuit board of the LSI chip for actuation and other connection between the electrode terminals of a minute pitch, recently, and gave conductivity is used, conductive ability especially with good altitude and repeatability is demanded of these application objects, and it waits for development of the conductive filler by which dispersibility has been improved more.

[0005] Since it is effective to adjust a size range in order to raise the dispersibility of conductive nonelectrolytic plating fine particles, preparing in the shape of [fixed] corpuscular character by sieving or grinding processing is also performed. However, even if it performs classification processing of high degree of accuracy, it is difficult to remove thoroughly the floc generated in the manufacture process, and the metal coat of the grain child front face which performs grinding processing breaks, and it causes lowering of conductive ability. Therefore, in order to obtain the nonelectrolytic plating fine particles which demonstrate the outstanding conductive ability, it is necessary to examine the shape of corpuscular character of the resin powder used

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[0012] As for the above-mentioned resin base material, spherical powder is substantially used as particle shape. It means including the configuration near a globular form like an ellipse form besides a perfect globular form substantially, as it is spherical, and the powder which presents the spherical gestalt which is in the range of 0.5-1.0 as a degree of sphericity of WADERU preferably is applicable. The degree of sphericity of WADERU shows that it is a particle near a real ball object, so that it is the characteristic measured by (equal to projected area of particle diameter-of-circle)/(the minimum diameter of circle circumscribed to the projection image of a particle) and this characteristic approximates the degree of sphericity of a particle to 1.0. Less than by 0.5, this degree of sphericity presents a protruding piece with a sharp powder configuration in many cases, and becomes the cause of spoiling the adhesion of a plating coat or making dispersibility declining.

[0013] As the shape of corpuscular character of a resin base material, mean particle diameter is 1-30 micrometers. The selection activity of 10% or less of the thing is carried out for the grain partial-volume ratio by the side of detailed among those for the grain which it is in the range, and the grain partial-volume ratio of  $\pm 20\%$  range of mean particle diameter occupied 70% or more, and separated from  $\pm 20\%$  range of mean particle diameter.

[0014] It is 1-30 micrometers about mean particle diameter. For the reason limited to the range, mean particle diameter is 1 micrometer. It is substantially difficult and it is 30 micrometers to obtain the super-very fine particle of the following. It is because specific surface area falls and conductive ability is made to decline, when it exceeds, the range of more desirable mean particle diameter — 5-10 micrometers it is. Whenever [grain / with which the grain partial-volume ratio in  $\pm 20\%$  of particle diameter range is less than 70% to this mean particle diameter], distribution broadcloth-izes and spoils uniform dispersibility. Moreover, if the grain partial-volume ratio by the side of detailed exceeds 10% among those for the grain which separated from  $\pm 20\%$  range of mean particle diameter, a very fine particle will increase, and it will become easy to produce condensation in a nonelectrolytic plating process, and will become the factor which reduces adhesion and dispersibility about a plating layer as a result. The grain partial-volume ratio by the side of detailed of more desirable particle size distribution is 1% or less among those for the grain in which the grain partial-volume ratio of  $\pm 20\%$  range of mean particle diameter is 90% or more, and separated from  $\pm 20\%$  range of mean particle diameter.

[0015] The metal coat by the electrodeless deposition method is formed in a front face at a resin base material equipped with the shape of above corpuscular character. The conductive metal which the metal to cover can nonelectrolytic plating operate, for example, Au, Ag, Co, Cu, nickel, Pd, Pt, Sn, etc., may be applicable, and these metals may be alloys and may be two or more sorts of double layer coats. However, for the object of this invention, it is desirable that a metal coat is nickel coat or a nickel-Au double layer coat. In being able to stick firmly with a base material resin particle and being able to form the good nonelectrolytic plating layer of peeling resistance, nickel coat has the profitableness which functions effectively as an interlayer who secures firm affinity with the upper plating coat layer, when carrying out the double stratification of the Au to the top face. Moreover, if it is made a nickel-Au double layer coat, compared with an independent coat, conductive ability can be raised further. With a monolayer coat, although the range of the thickness with the desirable nonelectrolytic plating layer to form is 10-300nm with 10-200nm and a double layer coat, it is not restricted to this.

[0016] The conductive nonelectrolytic plating fine particles concerning this invention use as a base material the resin powder substantially equipped with the spherical shape of specific corpuscular character. Catalyst-ized down stream processing which this is returned [down stream processing] and makes a base material side support palladium after making the front face of this base material catch palladium ion. A complexing agent can be added to the aqueous slurry of the base material which performed catalyst-ized processing, it can fully be distributed, and it can manufacture by giving the nonelectrolytic plating process which, subsequently to at least 2 liquid, carries out judgment addition of the metal nonelectrolytic plating liquid, and forms a metal coat. Moreover, in order to form a double layer coat, other metal nonelectrolytic plating is performed for the base material which formed the metal coat at the aforementioned process, and the approach of carrying out the coat of other metal coats to the top face of an initial metal

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as a plating base material, and to secure good dispersibility and adhesion.

[0006] this invention persons are substantially spherical as a base material, as a result of advancing examination on many sides about the shape of corpuscular character of the resin powder which serves as a plating base material from this viewpoint. If resin equipped with the shape of corpuscular character of the specific range is chosen and metallic coating is performed to this front face by the nonelectrolytic plating method, in forming the plating coat which was extremely excellent in adhesion, the data that the dispersibility over an object matrix component was improved effectively, and conductive advanced ability was always given were solved.

[0007] The place which this invention was developed based on the above-mentioned knowledge, and is made into the object is to offer the high-definition conductive nonelectrolytic plating powder which can give the dispersibility and high conductivity ability which were always excellent to the matrix component.

[0008]

[Means for Solving the Problem] The conductive nonelectrolytic plating fine particles by this invention for attaining the above-mentioned object it is a spherical particle substantially and mean particle diameter is 1-30 micrometers. It is in the range. The resin powder with which the grain part ratio by the side of detailed is equipped with the shape of 10% or less of corpuscular character among those for the grain which the grain part ratio of  $\pm 20\%$  range of mean particle diameter occupied 70% or more, and separated from  $\pm 20\%$  range of mean particle diameter is used as a base material. It is characterized by coming to form a metal coat in this base material front face by the nonelectrolytic plating method on a configuration.

[0009] In this invention, there is no constraint according to rank in the class of resin used as a nonelectrolytic plating base material. As usable resin, for example Polyethylene, a polyvinyl chloride, Polyolefines, such as polypropylene, polystyrene, and a polyisobutylene, Olefin copolymers, such as a styrene-acrylonitrile copolymer and an acrylonitrile-butadiene-styrene terpolymer, Acrylic-acid derivatives, such as polyacrylate, polymethylmethacrylate, and polyacrylamide, Polyvinyl compounds, such as polyvinyl acetate and polyvinyl alcohol, polyacetal, Ether polymers, such as a polyethylene glycol, a polypropylene glycol, and an epoxy resin, Benzoguanamine, a urea, thiourea, a melamine, acetoguanamine, The amino resin which consists of amino compounds, such as a cyanogen amide and an aniline, and aldehydes like formaldehyde, a paraformaldehyde, an acetaldehyde, and glyoxal, polyurethane, polyester, a fluorine-containing resin, nitril system resin, etc. can be mentioned. However, in these, the styrene resin represented by benzoguanamine system resin, such as for example, benzoguanamine formaldehyde resins or benzoguanamine melamine-formaldehyde resin, or polystyrene resin is used suitably.

[0010] Among these, benzoguanamine system resin can be manufactured by the approach currently indicated by JP.46-9420B, JP.52-27679B, JP.52-18594A, or JP.52-51493A. Specifically add in formalin the mixture which consists of benzoguanamine or benzoguanamine, and a melamine, and pH is adjusted to 5-10. Make it react until a resultant carries out hydrophobing at the temperature of 50-100 degrees C, and a protective colloid solution suitable after reaction termination is made to emulsify by the quantitative ratio of 1-30 weight section to the resultant 100 weight section in addition to the bottom of churning. Subsequently, it can obtain as a spherical particle minutely and substantially under existence of a polymerization catalyst by the approach of carrying out polymerization hardening in the state of emulsification at the temperature of 50-100 degrees C.

[0011] On the other hand, although styrene resin is a polymer which makes styrene a subject, you may be the cross linked polymer by copolymerization of styrene and a small amount of polyfunctional monomer. As styrene and a copolymerizable monomer, acrylic ester, methacrylic ester, unsaturated carboxylic acid, acrylonitrile, PUTAJEN, etc. are mentioned. The polyfunctional monomer which copolymerizes and forms the cross linked polymer is JI or Tori (meta) acrylic ester of for example, JIBINI benzene and polyhydric alcohol etc. Spherical styrene resin powder can be obtained minutely and substantially by agitating under heating the mixed liquor which added these monomers, the radical polymerization initiator, and the suspension stabilizer.

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plating layer is taken.

[0017] The concrete means of a nonelectrolytic plating method is performed as follows. First, refining processing which gives catalyst prehension ability to the front face of the base material resin particle used as a base material is performed. Catalyst prehension ability is a function in which a base material front face can catch palladium ion as a chelate or a salt in catalyst-ized down stream processing, and refining-ization can be performed using the epoxy system resin hardened with an approach, i.e., an amine-group permutation organosilane system coupling agent, and an amine system curing agent given in JP.61-64892A.

[0018] Catalyst-ized down stream processing is performed by the approach of carrying out reduction processing of the palladium ion which the thin aqueous acids of a palladium chloride were made fully distributing the base material which gave catalyst prehension ability by refining-ization, was made catching palladium ion on a front face, and was subsequently made catching, and making the front face of a base material particle supporting palladium. Under the present circumstances, the concentration of a palladium-chloride water solution is 0.05-1 g/l. It considers as the range and sodium hypophosphite, hydroxylation boron sodium, a hydrogenation boron potassium, dimethylamine borane, a hydrazine, or formalin is used for a reducing agent. The addition of a reducing agent is [as opposed to / in general / a water solution] 0.01-10 g/l, although it changes with particle size of a base material. The range is suitable.

[0019] the base material particle to which the nonelectrolytic plating process performed catalyst-ized processing as the 1st step — water — enough — homogeneity — distributing — distributed concentration — 2-500 g/l — desirable — 5-300 g/l An aqueous slurry is prepared. It can usually carry out to distributed actuation using churning, high-speed churning, a colloid mill, or shearing distribution equipment like a homogenizer. Subsequently, a complexing agent is added to an aqueous slurry and it is fully distributed. As a complexing agent, at least one sort of the compound which has a complexing operation to metal ions, such as amine acids, such as amino acid, such as carboxylic acid (salt), such as a citric acid, hydroxyacetic acid, a tartaric acid, a malic acid, a lactic acid, a gluconic acid or its alkali-metal salt, and ammonium salt, and a glycine, ethylenediamine, and alkylamine, other ammonium, EDTA, and a pyrophosphoric acid (salt), is used, for example, although a complexing agent is usually added in the state of a water solution — the concentration — 1-100 g/l — desirable — 5-50 g/l It is set as the range. The range of pH of the desirable aqueous slurry in this phase is 4-14.

[0020] Thus, a nonelectrolytic plating reaction is performed to the prepared aqueous slurry by using each water solution of a metal salt, sodium hypophosphite, and a sodium hydroxide as at least 2 liquid, and carrying out judgment addition respectively individually and simultaneous as nonelectrolytic plating liquid. Although a plating reaction will start promptly if nonelectrolytic plating liquid is added to an aqueous slurry, the metal coat formed by adjusting the addition is controllable to desired thickness. After addition termination of nonelectrolytic plating liquid, holding solution temperature for a while, since generating of hydrogen gas is no longer accepted thoroughly, churning is continued and a reaction is completed.

[0021] Although a metal coat is dense and is formed as a continuous thin film of the above-mentioned process, the double layer coat which is further excellent in conductive ability can be formed by performing other metal plating processings to the front face further, for example, warming which adjusted pH to a complexing agent like EDTA-4Na and citric-acid-2Na, and the gold cyanide potassium to the weak acidic field in the sodium-hydroxide water solution in formation of Au coat — in nonelectrolytic plating liquid it is performed by the actuation which adds separately the mixed water solution of a gold cyanide potassium, EDTA-4Na, and citric-acid-2Na, and the mixed water solution of a hydrogenation boron potassium and a sodium hydroxide, and carries out a plating reaction, after adding agitating said plating powder and considering as distributed suspension. Hereafter, it collects as a product by carrying out after treatment with a conventional method similarly.

[0022] Thus, the conductive nonelectrolytic plating fine particles to which metallic coating was performed by the nonelectrolytic plating method have a precise coat metal layer, and since it is formed as a thin film of a continuity, the shape of the corpuscular character does not bring a difference substantially to particle size distribution etc. with extent to which particle size

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becomes large slightly compared with a base material resin particle.

[0023]

[Function] This invention as resin powder used as the base material which carries out nonelectrolytic plating of the conductive metal. The shape of particle presents the shape of a ball substantially, and mean particle diameter is 1-30 micrometers. It is in the range. The main descriptions are that it carried out the selection activity of what the grain partial-volume ratio by the side of detailed equips with the shape of 10% or less of corpuscular character among those for the grain which the grain partial-volume ratio of \*\*20% range of mean particle diameter occupied 70% or more, and separated from \*\*20% range of mean particle diameter.

[0024] Among these, substantially, the spherical shape of particle has the outstanding fluidity, and while preventing the phenomenon which each particles of both condensation-size, in order to form a uniform plating layer, it functions effectively. Mean particle diameter of 1-30 micrometers. The range contributes in order to raise conductive ability, when a matrix is made to carry out distributed compound of the nonelectrolytic plating fine particles as a very fine particle with a big specific surface area. The amount of [ to which 10% or less of definition has sharp particle size distribution, and the grain partial-volume ratio by the side of detailed promotes condensation-ization among those for the grain which the grain partial-volume ratio of \*\*20% range of mean particle diameter occupied 70% or more, and separated from \*\*20% range of mean particle diameter ] detailed grain has the shape of little corpuscular character relatively, and the operation which improves the dispersibility of plating fine particles remarkably is performed at the same time it raises the adhesion of a nonelectrolytic plating metal. Such an operation becomes possible [ offering the nonelectrolytic plating fine particles which can always blend with sufficient dispersibility to a matrix material, and can perform grant of high conductivity ability conjointly ].

[0025]

[Example] Hereafter, the example of this invention is concretely explained as contrasted with the example of a comparison.

[0026] Examples 1-5 and examples 1-4 of a comparison (1) Base material resin powder; the degree of sphericity of WADERU used 0.5 or more the benzoguanamine formaldehyde resins (BA), benzoguanamine melamine-formaldehyde resin (BMA), and polystyrene resin (PS) of the shape of corpuscular character which is spherical powder substantially and is shown in a table 1 as a base material.

[0027]

[A table 1]

例No.	基材樹脂	平均粒子径 (μm)	平均粒子径±20% 範囲の粒分率比 (%)	平均粒子径±20% 範囲外の粒分率比 (%)
実例1	BA	7.8	99.5	0.5
2	BA	4.6	99.0	0.4
3	BMA	7.8	99.5	0.5
4	BMA	4.6	99.0	0.4
5	PS	10.3	80.2	2.30
比較例1	BA	9.6	44.7	25.6
2	BMA	15.4	59.5	14.8
3	BMA	3.3	59.2	13.8
4	PS	9.2	36.1	33.8

[Front notes] BA: benzoguanamine formaldehyde resins, BMA: BENZOQUA NAMIN melamine-

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formaldehyde resin, PS; polystyrene resin.

[0028] (2) nickel nonelectrolytic plating processing; 10g of each base material resin powder of a table 1 is supplied agitating in 200ml of conditioner liquid [product made from SHIPURE] and the "cleaner conditioner 231" 40 ml/l water solutions, churning processing was successively carried out for 5 minutes, and surface treatment was performed. It is the base material resin powder which filtered the water solution and carried out RIPAUBU rinsing once 1 g/l of ordinary temperature. It was immersed in 200ml of stannous chloride water solutions for 5 minutes, it filtered and washed, and sensitization processing was performed. Subsequently, it supplied agitating in 200ml of catalyst-sized liquid which consists of a 0.1 ml/l palladium-chloride water solution and a hydrochloric acid of 0.1 ml/l, churning processing was successively carried out for 5 minutes, and palladium ion was made to catch. They are the base material fine particles which filtered the water solution and carried out RIPAUBU rinsing once 1 g/l of ordinary temperature. It was immersed in the sodium hypophosphite water solution for 5 minutes, reduction processing was performed, and the base material front face was made to support palladium. It added agitating in each complexing agent water solution which shows a base material in the table 2 warmed in temperature of 65 degrees C, and after fully carrying out churning distribution and preparing an aqueous slurry, it added simultaneously, having divided into a liquid and b liquid nickel nonelectrolytic plating liquid shown in a table 3, and agitating 80ml at the addition rate for 5ml/respectively.

[0029]

[A table 2]

例No.	緑化剤の種類	濃度(g/l)	pH
実例1	リンゴ酸ソーダ	1.0	6
2	グリシン	2.0	8
3	酢石炭ソーダ	1.0	7
4	クエン酸ソーダ	5	7
5	炭酸ソーダ	2.0	6
比較例1	リンゴ酸	1.0	6
2	リンゴ酸	1.0	6
3	酢石炭ソーダ	1.0	7
4	酢石炭ソーダ	1.0	7

[0030]

[A table 3]

N1 電解液めっき液の組成	濃度(g/l)	モル比
a液: 硫酸ニッケル	2.24	1
b液: 水素還元剤ナトリウム	2.26	2.5
水酸化ナトリウム	1.19	3.5

[0031] Churning was continued after adding the whole quantity of nickel nonelectrolytic plating liquid, holding the temperature of 65 degrees C until foaming of hydrogen stopped. Subsequently, plating liquid was filtered and the powder which dries at 100 degrees C with a vacuum dryer, and has nickel coat after carrying out RIPAUBU washing of the filtration object 3 times was obtained. Each filtrate after a plating reaction is transparent and colorless, and what the offered

[http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\\_web.cgi.eje](http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.eje)

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plating liquid was thoroughly consumed for by the plating reaction was accepted. When observed with the electron microscope about obtained nickel nonelectrolytic plating particle, flocc was an independent particle which hardly exists, it is a spherical particle substantially, and the plating coat was dense and the thing whose all present the homogeneous and smooth enveloping layer by detailed nickel metal particles and which is formed as a continuous coat was checked.

[0032] (3) Au nonelectrolytic plating processing; in 10.0g of nickel nonelectrolytic plating particles obtained at the above-mentioned process, they are EDTA-4Na (10 g/l) and citric-acid-2Na (10 g/l). And it added agitating in the nonelectrolytic plating liquid (A liquid) of 60 degrees C of solution temperature adjusted to pH6 with the sodium-hydroxide water solution by the presentation which consists of a gold cyanide potassium (3.0 g/l, 2.1 g/l as Au), and Au plating processing during 10 minutes was performed. Subsequently, a gold cyanide potassium (10 g/l, 6.8 g/l as Au) and EDTA-4Na (10 g/l) And citric-acid-2Na (10 g/l) A mixed water solution (B liquid), and a hydrogenation boron potassium (30 g/l) and a sodium hydroxide (80 g/l) The mixed water solution (C liquid) was added in 20 minutes individually and simultaneous through the liquid-sending pump. A volume, B volume, and C volume in this case were set as the quantitative ratio shown in a table 4.

[0033]

[A table 4]

例No.	A液量 (ml)	B液量 (ml)	C液量 (ml)
実例1	152	47	47
2	255	79	79
3	152	47	47
4	255	79	79
5	152	47	47
比較例1	152	47	47
2	152	47	47
3	152	47	47
4	152	47	47

[0034] Then, liquid was filtered, after carrying out RIPAUBU washing of the filtration object 3 times, it dried at the temperature of 100 degrees C with hot air drying equipment, and Au nonelectrolytic plating coat processing was performed on nickel coat, and the double layer coat of nickel-Au was formed in the base material side, electron microscope photograph (scale factor, about 330 times) in which the particulate structure of the conductive nonelectrolytic plating fine particles (mean particle diameter, 4.84 micrometers) by the double layer coat of nickel-Au from which drawing 1 was obtained according to the example 2 was shown it is -- electron microscope photograph (scale factor, about 330 times) in which the particulate structure of the conductive nonelectrolytic plating fine particles (mean particle diameter, 9.8 micrometers) by the double layer coat of nickel-Au from which drawing 2 was obtained by the example 4 of a comparison was shown it is.

[0035] (3) Physical-properties assessment; measurement assessment of the thickness of the mean particle diameter of the conductive nonelectrolytic plating fine particles obtained by doing in this way and nickel coat after nickel nonelectrolytic plating processing and conductivity, dispersibility, peeling resistance, and a nickel-Au double layer coat and conductivity, dispersibility, and the peeling resistance was carried out, respectively, and the result was shown in a table 5 and a table 6. In addition, each physical-properties assessment was performed by the following approach.

[0036] \*\* Measurement of the mean particle diameter of plating fine particles; it measured by

the Coulter counter method and the laser diffraction method.

\*\* Calculation of plating thickness; plating thickness was computed by the bottom type.

$$A = \frac{[(r + t)^3 - r^3] \cdot d}{t \cdot d}$$

However, r Radius of a base material particle (micrometer) t Plating thickness (micrometer) d1 is the specific gravity of the plating film, and d2 is the specific gravity of a base material particle.

\*\* Conductive measurement; 1.5g of plating powder it put in the cylinder made of resin with a bore of 10mm stood vertically, and carried out by the approach of measuring electric resistance vertical inter-electrode with the condition of having applied the 5kg load.

[0037] \*\* Measurement of dispersibility; 0.1g of plating powder it processes for 1 minute by ultrasonic washing machine [Honda Electronics Co., Ltd. make, 28kHz, and 100W, putting into a 100ml beaker, adding toluene 50ml, and stirring with a micro spatula. The processed slurry is extended to extent which serves as a diameter of 1cm on ejection and slide glass with a micro spatula. Slide glass is set to the base of a metaloscope (made in Olympus, 500 times), and the situation 1 minute after irradiating the transmitted light is photoed. The assessment approach measures the number which the plating particle is condensing in the magnitude of 5 times or more in the length and the longitudinal direction of mean particle diameter by photograph 20 visual field photoed by the above-mentioned approach, and carries out an assessment judging on the following criteria.

Five or less pieces -- 0 5-10 pieces -- 0 Ten or more pieces -- x [0038] \*\* Measurement of

adhesion; 2.2g [ of plating powder ], and zirconia-beads 90g it puts into a 100ml mayonnaise bottle, and toluene 10ml is added with a transfer pipet. It is 400rpm during 10 minutes with an agitator (three one motor). It agitates for 10 minutes. The sample solution is sucked up with a pipet after termination, and it extends so that it may become the diameter of about 1cm on a slide. After toluene evaporates, one drop of dispersant is hung down and it extends to homogeneity by Spa Zikah. 5 visual-field transparency photography (500 times) is observed and carried out with a metaloscope, the visual field that plating layer exfoliation is the most intense is observed, and the following criterion estimates from the number of exfoliations.

Two or less pieces -- 0 2-10 pieces -- 0 Ten or more pieces -- x [0039] Dry grinding was performed until particle distribution almost equivalent to a base material particle was shown in the ball mill into which alumina balls were put for the nonelectrolytic plating fine particles produced in the example 1 of example of comparison 5 comparison, measurement assessment of the description of fine particles was carried out, and it carried jointly in a table 5 and a table 6.

[0040]

[A table 5]



例No.	N i 無電解めっき粉体の物性				
	平均粒子径 ( $\mu\text{m}$ )	膜 厚 ( $\text{nm}$ )	電気抵抗値 ( $\Omega\text{cm}$ )	分散性	密着性
実施例 1	8.1	115	$1.2 \times 10^{-4}$	○	○
・ 2	4.9	97	$3.2 \times 10^{-4}$	○	○
・ 3	7.9	121	$1.0 \times 10^{-4}$	○	○
・ 4	5.1	113	$4.8 \times 10^{-4}$	○	○
・ 5	14.7	152	$1.8 \times 10^{-4}$	○	○
比較例 1	20.9	150	$2.9 \times 10^{-4}$	×	○
・ 2	31.9	290	$4.0 \times 10^{-4}$	×	○
・ 3	13.2	110	$2.9 \times 10^{-4}$	×	○
・ 4	10.0	150	$7.2 \times 10^{-4}$	○	×
・ 5	23.6	170	$2.0 \times 10^{-4}$	×	○

[0041]

[A table 6]

例No.	N i - A u 無電解めっき粉体の物性				
	平均粒子径 ( $\mu\text{m}$ )	膜 厚 ( $\text{nm}$ )	電気抵抗値 ( $\Omega\text{cm}$ )	分散性	密着性
実施例 1	8.2	20	$2.0 \times 10^{-4}$	○	○
・ 2	4.84	22	$3.0 \times 10^{-4}$	○	○
・ 3	8.0	20	$1.0 \times 10^{-4}$	○	○
・ 4	4.82	20	$2.0 \times 10^{-4}$	○	○
・ 5	17.0	20	$0.9 \times 10^{-4}$	○	○
比較例 1	23.6	13	$1.0 \times 10^{-4}$	×	○
・ 2	44.0	20	$1.0 \times 10^{-4}$	×	○
・ 3	15.8	21	$2.0 \times 10^{-4}$	×	○
・ 4	9.8	13	3.5	○	×
・ 5	29.4	20	$1.0 \times 10^{-4}$	×	○

[0042] From the result of a table 5 and a table 6, the conductive nonelectrolytic plating fine particles by the example are excellent in conductivity, dispersibility, and adhesion compared with the example of a comparison which separates from the requirements for this invention, and it is admitted that especially dispersibility is improved remarkably.

[0043] Example 6 (1) Ag nonelectrolytic plating processing: the same benzoguanamine formaldehyde-resins powder as the example 1 shown in a table 1 is used as a base material, and it is 10g of this resin powder. It supplied agitating in 200ml of conditioner liquid [product made from SHIPURE] and the "cleaner conditioner Z31" 40 ml/l water solutions, churning processing was successively carried out for 5 minutes, and surface treatment was performed. It is the base material powder which filtered the water solution and carried out repulping rinsing once 1 g/l of

ordinary temperature It was immersed in 200ml of stannous chloride water solutions for 5 minutes, it filtered and washed, and sensitization processing was performed. Subsequently, it supplied agitating in 200ml of catalyst-sized liquid which consists of a 0.1 ml/l palladium-chloride water solution and a hydrochloric acid of 0.1 ml/l, churning processing was successively carried out for 5 minutes, and palladium ion was made to catch. It is the base material powder which filtered the water solution and carried out RIPARUBU rinsing once 1 g/l of ordinary temperature It was immersed in the sodium hypophosphite water solution for 5 minutes, reduction processing was performed, and the base material front face was made to support palladium. Subsequently, a sodium hydroxide and a sodium cyanide 4g [1.] each It was made to distribute in the liquid which warmed the included liquid at 80 degrees C, and it added simultaneously, having divided into a liquid and b liquid Ag nonelectrolytic plating liquid shown in a table 7 like an example 1, and agitating 80ml at the addition rate for 5ml/respectively.

[0044]

[A table 7]

Ag 無電解めっき液の組成	濃度 (g/l)	モル比
a 液 ; シアン化銀カリウム	150	1
b 液 ; 水酸化ホウ素ナトリウム	36	1.2
水酸化ナトリウム	120	4.0

[0045] After adding the whole quantity of Ag nonelectrolytic plating liquid, churning was continued holding the temperature of 65 degrees C until foaming of hydrogen stopped. Subsequently, plating liquid was filtered, repulping washing of the filtration object was carried out 3 times, and the powder which dries at 100 degrees C with a vacuum dryer, and has Ag coat was obtained. Each filtrate after a plating reaction is transparent and colorless, and what the offered plating liquid was thoroughly consumed for by the plating reaction was accepted. When observed with the electron microscope about obtained Ag nonelectrolytic plating particle, it is the spherical particle which all present the homogeneous and smooth enveloping layer by detailed Ag metal particles, and it was checked that a plating coat is dense and is substantially formed as a continuation coat.

[0046] (2) Au nonelectrolytic plating processing: above (1) Non-electrolyzed Au plating processing was performed by the example 1 and identity operation to Ag non-electrolyzed silver plating processing fine particles obtained at the process.

[0047] Thus, various kinds of physical properties were evaluated for the conductive nonelectrolytic plating fine particles which have the obtained Ag-Au double layer coat like the example 1, and the result was shown in a table 8.

[0048] Replacing example 7 base-material resin powder with the same benzoguanamine formaldehyde resins as an example 2, others produced the conductive nonelectrolytic plating fine particles which have an Ag-Au double layer coat by the same actuation as an example 6. Various kinds of physical properties were evaluated for these conductive nonelectrolytic plating fine particles like the example 1, and that result was carried jointly in a table 8.

[0049] As example of comparison 6 base material, it is the mean particle diameter of 9.8 micrometers. The grain partial-volume ratio of  $\pm 20\%$  range of mean particle diameter produced the conductivity nonelectrolytic plating [ which has an Ag-Au double layer coat by the same actuation as an example 6, using spherical benzoguanamine melamine-formaldehyde resin powder substantially ] fine particles whose grain partial-volume ratio by the side of detailed is 25.6% 44.7% among those for the grain which separated from  $\pm 20\%$  range of mean particle diameter. Various kinds of physical properties were evaluated for these conductive nonelectrolytic plating fine particles like the example 1, and that result was carried jointly in a table 8.

[0050]

[A table 8]

例No.	Ag-Au 無電解めっき粉体の物性					
	平均粒子径 ( $\mu\text{m}$ )	膜 厚 (nm)		電気抵抗値 ( $\Omega\text{cm}$ )	分散性	密着性
		Ag	Au			
実施例6 ・ 7	8.2	100	21	$1 \times 10^{-4}$	○	○
	4.7	88	21	$1 \times 10^{-4}$	○	○
比較例6	31.4	110	22	$1 \times 10^{-4}$ 以下	×	○

[0051]

[Effect of the Invention] As above, when it is substantially spherical as a base material according to this invention and particle size distribution cover a non-electrolyzed metal plating layer on a front face using the particle resin powder of the sharp specific range, it becomes possible to offer the conductive nonelectrolytic plating fine particles which a precise and continuous plating layer covers with sufficient adhesion, and are excellent in the dispersibility over a compound matrix material. It is very useful for the application as which it follows, for example, conductive advanced ability like the precision electric conduction material for liquid crystal display panels is required.

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[Translation done.]

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## DESCRIPTION OF DRAWINGS

## [Brief Description of the Drawings]

[Drawing 1] electron microscope photograph (scale factor; about 330 twice) in which the particulate structure of the conductive nonelectrolytic plating fine particles (mean particle diameter; 4.84 micrometers) by the double layer coat of nickel-Au obtained according to the example 2 was shown it is .

[Drawing 2] electron microscope photograph (scale factor; about 330 twice) in which the particulate structure of the conductive nonelectrolytic plating fine particles (mean particle diameter; 9.8 micrometers) by the double layer coat of nickel-Au obtained by the example 4 of a comparison was shown it is .

[Translation done.]

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